Coulomb Energy Determination of a Single Si Dangling Bond

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Determination of the Coulomb energy of single point defects is essential because changing their charge state critically affects the properties of materials. Based on a novel approach that allows us to simultaneously identify a point defect and to monitor the occupation probability of its electronic state, we unambiguously measure the charging energy of a single Si dangling bond with tunneling spectroscopy. Comparing the experimental result with tight-binding calculations highlights the importance of the particular surrounding of the localized state on the effective charging energy.

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Real crystals universally contain point defects. Such imperfections alter the perfect crystal's chemical bonds, its lattice stability, and the atomic geometry, giving rise to one or several localized states in the band gap of all semiconductor and insulating materials. These states provide electron trapping sites, which can be empty or occupied depending on the electrochemical potential. Understanding the change of the charge state of single point defects is thus crucial, because it governs many important properties of materials, such as their conductivity [1,2], color [3,4], chemical reactivity [5,6], and the diffusion of atoms [7,8].

Adding an electron to a point defect that has already trapped one electron requires overcoming the Coulomb energy U. Because of the strong localization of the defect state, U can be substantial, of the order of a few eVs [9]. Knowing U is thus of fundamental importance to determine the physical properties of materials. Experimentally, techniques such as deep level transient spectroscopy, capacitance measurements, and optical experiments allow the determination of U. But all these techniques probe the macroscopic properties of a sample and cannot simultaneously characterize the nature of point defects and measure the Coulomb interaction. This is particularly true for the Si dangling bond (DB), the major defect in amorphous Si and at the Si/SiO_2 interface [10].

In the past decade, STM has played a central role in the identification of numerous point defects, on surfaces, interfaces and the bulk [11]. Based on this method, we describe a general approach to determine the Coulomb energy of a single point defect. As a prototypical example, we consider a Si DB, where long-standing controversies exist about the value of U [12,13]. Isolated Si DBs are found on the B-doped Si(111)-$(\sqrt{3} \times \sqrt{3})R30°$ surface [14]. Transport through their nonresonant ground state is a two-step process that involves the tunneling of an electron between a tip state and the DB state and, then, the nonradiative recombination of the electron with a hole from the valence band [15]. When the tunneling rate becomes higher than the hole capture rate, the inelastic current saturates [16], suggesting that charging with a second electron is, in principle, possible.

However, the energy dependence of the transmission probability to transfer an electron through a single energy level weakly coupled to the leads generally results in a reduction of the tunneling rate for energies above the DB ground state [17]. Therefore the occupation probability of the DB cannot be kept constant when the sample voltage increases, preventing the defect from changing its charge state. In order to overcome such a deadlock, we adopt a new experimental scheme, where we probe the transition between the shell-tunneling and shell-filling regimes by performing tunneling spectroscopic measurements with the feedback control loop on. From the disappearance of the first excited state of the neutral DB and the emergence of a new peak resonant with the conduction band, we demonstrate the two-electron charging of a single DB. The measurement of U is corroborated by tight-binding calculations that take into account the proximity of the tip.

The experiments were carried out on a B-doped Si(111) surface held at 5 K. Because of the segregation of B atoms during the surface preparation at temperatures higher than 900 °C, B impurities replace Si atoms located just under the Si adatom position, causing the passivation of the DB states of the Si adatoms [18]. For a few atomic sites, however, the substitution does not take place, leading to the occurrence of bright adatoms in the empty state STM image of the surface. Such a bright adatom is clearly seen in Fig. 1(b), its contrast arising from the localized state of the DB in the Si band gap [15]. In principle, the DB state can be occupied by $n = 0$, 1, or 2 electrons corresponding to $+$, 0, and $-$ charge states, respectively.

To study the electronic configurations of the DB, tunneling spectroscopy was performed with a lock-in amplifier. As shown in Fig. 1(a), we measure the position of the conduction band edge E_C at an energy of $+1.11$ eV above

the Fermi level [curve (iii)]. On a bright adatom [curve (i)], a prominent peak, followed by a minimum at higher voltage, both in the Si band gap, reveals a negative differential resistance behavior. The linewidth of the peaks is related to the strong excitation of vibrational states [15].

Interestingly, measurements performed on the first adatom neighbors of a bright adatom [curve (ii)] show one peak positioned just below E_C, at 1.05 V. This peak has not been noticed in previous studies, and its sharp linewidth (limited by the amplitude of the modulation: 6 meV) readily contrasts with the broad peak observed on a bright adatom. Mapping out the electron density at the energies of the positive broad peak and the sharp peak also reveals a significant difference in the spatial extent of the square of the wave function related to both states. While the electronic state corresponding to the broad peak is strongly localized on the bright adatom in agreement with the radius expected for a deep state [16], the state related to the sharp peak extends over a few atomic sites around the bright adatom.

These observations can be understood as follows. Because of the high concentration of B acceptors in the sample (resistivity 1 m$\Omega \cdot$ cm), the Fermi level is positioned at the top of the valence band. Therefore, the DB is positively charged ($n = 0$) until an electron is transferred from the tip so that the DB becomes neutral ($n = 1$). The broad peak thus corresponds to the $(+/0)$ transition [Fig. 2(a)]. As in the experiment of Fig. 1 the intensity of the current transferred through the DB is much smaller than the intensity required to saturate the current [16], the DB remains positively charged on average. It thus induces a screened Coulomb potential that attracts a hydrogenic-like state below E_C. From the wave function mapping, the weight of the wave function for this state related to the sharp peak is zero at the position of the bright adatom. This wave function is thus orthogonal to the ground state of the neutral DB. Therefore we identify the sharp peak as the level $(+/0^*)$ for the transition from the positive charge state to the first excited state of the neutral DB [Fig. 2(a)]. The sharp linewidth of the peak is consistent with a state that cannot couple to the main vibrational mode of the Si adatom, because the wave function is zero at the position of the Si adatom. In addition, its localization is consistent with the spatial extent of shallow levels measured by tunneling spectroscopy of other semiconductor dopants [19,20].

By increasing the tunneling current set point, the current transferred through $(+/0)$ increases and finally saturates. Such behavior is clearly seen in Fig. 2(b), where, for the DB studied in this case, saturation is measured for a current set point of 35 nA. In the permanent regime, the current though $(+/0)$ is given by $I_{(+/0)} = -e(1-f)W$, where W is the tunneling rate between the tip and the DB and f is the occupation probability of the DB state [21]. As I must equal the current generated from the capture of the hole by the DB, we obtain from the intensity at

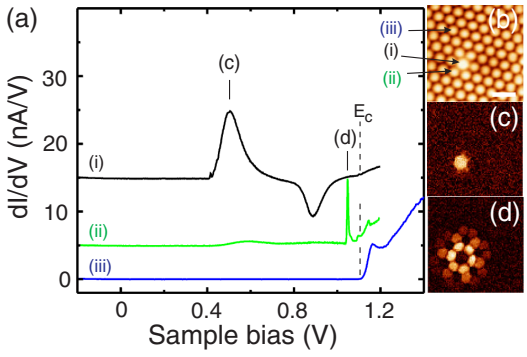

FIG. 1 (color online). (a) Differential conductance spectra measured on (i) a nonpassivated bright Si adatom, (ii) one of its six first neighbors, and (iii) a passivated Si adatom. (Tunneling current $I_t = 0.6$ nA, $V_{\mathrm{mod}} = 6$ mV$_{p-p}$, and $f_{\mathrm{mod}} = 495$ Hz.) The conduction band edge is labeled E_c. (b)–(d) Spatially resolved tunneling spectroscopic measurements obtained on a bright adatom: (b) topographic image (sample voltage $V_s = +1.60$ V, $I_t = 3.0$ nA, scale bar 1 nm), (c),(d) dI/dV conductivity maps measured at $V_s = +0.50$ and $+1.05$ V, respectively.

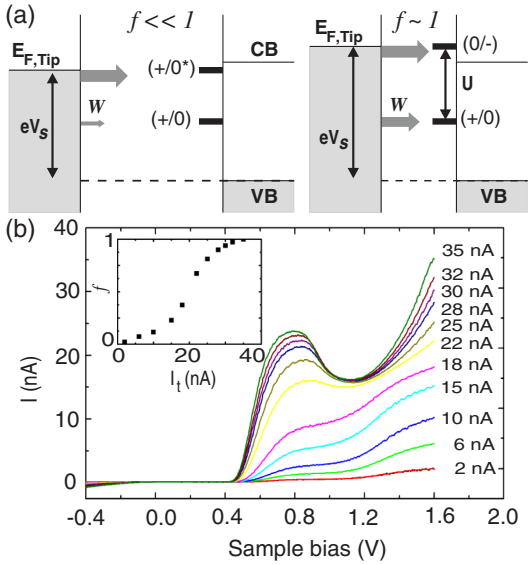

FIG. 2 (color online). (a) Available electronic states of a nonpassivated dangling bond as a function of the occupation probability f. At large tip-sample distances, f is small and the DB is positively charged on average. Electrons tunnel from tip states below the tip Fermi level to the DB ground state and first excited state giving rise to the transitions $(+/0)$ and $(+/0^*)$, respectively. At small tip-sample distances, f is close to 1 and the DB ground state is continuously occupied. The degeneracy of DB_0 is lifted. Electrons are transferred at transition levels $(+/0)$ and $(0/-)$. The tunneling rates through the different states are indicated by arrows, and the rate through the DB ground state is labeled W. The valence and conduction bands, tip Fermi level, sample bias, and effective intra-atomic Coulomb repulsion energy are, respectively, labeled VB, CB, $E_{F,\mathrm{Tip}}$, V_S, and U. (b) Tunneling current spectra measured on a bright Si adatom for different set point currents at $V_S = +1.6$ V. Inset: Variation of f with respect to the tunneling current set point.

saturation $f = I_{(+/0)}/I_{\mathrm{Max}}$, with $I_{\mathrm{Max}} = -ec_p p$, c_p and p being the hole capture coefficient of the DB and the hole concentration, respectively [16].

Measuring the current transferred through the DB for each current set point allows us to plot the variation of f [inset in Fig. 2(b)]. When the tip-sample distance is large, W is small in comparison with $c_p p$, and f is close to zero, corresponding to a predominantly positively charged DB. Conversely, when W is higher than $c_p p$, f approaches unity, and the DB is continuously occupied with one electron (i.e., neutral). In this regime, the transfer of a second electron into the DB should give rise to a second peak $(0/-)$ that is separated from $(+/0)$ by an energy estimated in the range 0.2–1.2 eV, depending on the environment of the Si DB [12,22]. However, no second peak is visible between 0.8 and 1.6 V in Fig. 2(b).

Interestingly, the tunneling current decreases once the tip Fermi level becomes higher than the level $(+/0)$, measured at $V_s = 0.79$ V for a set point current of 35 nA [Fig. 2(b)]. Such an effect occurs because the electrons continue to tunnel at the energy of $(+/0)$ from states below the tip Fermi level, and the probability of that tunneling decreases since the transmission is strongly peaked near the tip Fermi level [14]. Therefore, at constant tip-sample separation, the condition that the DB is continuously filled with one electron is never fulfilled when the tip Fermi level is higher than $(+/0)$. In this respect, tunneling through $(0/-)$ is unlikely to occur unless the current at saturation is maintained constant for energies above $(+/0)$.

In order to circumvent this limitation, spectroscopic measurements have been performed with a closed feedback loop. In this regime the tunneling current is kept constant by approaching the tip toward the surface in order to cancel any decrease of W, while the tip Fermi level is shifted above $(+/0)$. In these conditions, there is a continuous occupation of the DB with one electron which prevents the injection of an electron through $(+/0^*)$ (first excited state of the neutral DB). This behavior can be clearly seen in the variations of the $(+/0^*)$ peak intensity with respect to the tunneling current set point when measured on the first neighbors of the bright adatoms.

Figure 3 gives an example of such measurements. The constant-current differential conductance is measured at a frequency higher than the cutoff frequency of the feedback loop. Whatever the tunneling set point current is, the current could be maintained constant between 0.8 and 1.0 V, due to the tunneling of electrons into the tail of the DB ground state. At small set point currents, a step and a sharp peak are clearly visible in the $Z(V)$ and $dI(V)/dV$ spectra, respectively, corresponding to $(+/0^*)$. With increasing set point currents, the step in $Z(V)$ quickly disappears and is replaced by a smoother and more intense step that we attribute to the edge of the conduction band. In the $dI(V)/dV$ spectra, the peak related to $(+/0^*)$ is still resolved, but its intensity decreases. Such a decrease is

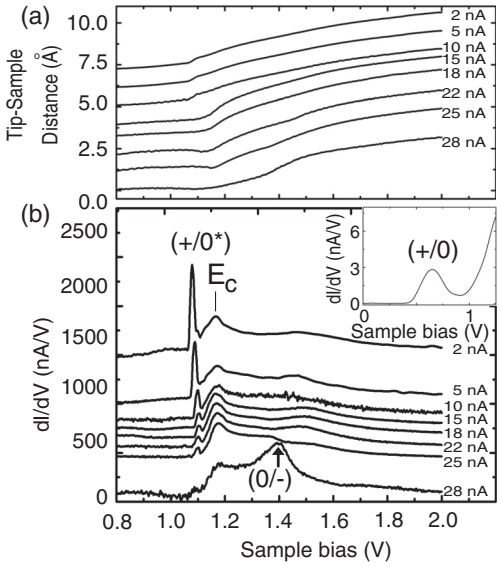

FIG. 3. Spectroscopic measurements performed on the first neighbor of a bright Si adatom for different tunneling set point currents. The feedback loop was maintained close to keep the current constant and thereby filling continuously the DB ground state even at larger voltages. Variation of (a) the tip-sample distance and (b) the differential conductance as a function of the sample bias ($f_{\mathrm{mod}} = 2.0$ kHz). The peaks labeled $(+/0)$, $(+/0^*)$, and $(0/-)$, respectively, correspond to the transition from the positive charge state to the ground state of the neutral DB, the positive charge state to the first excited state of the neutral DB, and the neutral DB to the second electron excitation of the ground state. E_c indicates the bottom of the conduction band. The spectra were averaged, except for the data corresponding to $I_t = 10$ nA, where a single curve was acquired. Inset: dI/dV acquired on the same bright Si adatom with the feedback switched off to measure $(+/0)$ ($V_S = +1.6$ V, $I_t = 2$ nA).

consistent with an increase of f, preventing the excited states from being further filled. For a set point current of 22 nA, a new downward step emerges below +1.4 V. For $I_t = 28$ nA, this step turns into a strong peak, while the signal becomes more noisy for voltages below this peak. We attribute this peak to the transition $(0/-)$. From the position of $(+/0)$ [inset in Fig. 3(b)], we deduce $\Delta E = E(0/-) - E(+/0) = 0.75$ eV, consistent with the expected values. The energy separation ΔE for the other bright Si adatoms probed on the same surface is similar within ± 0.05 eV, the uncertainty certainly resulting from the environment of the Si DB [16].

It remains to relate ΔE to U. The total energy of the DB occupied by n electrons can be written as [22]

$$E(n, Q) = n\varepsilon_0 + Un^2/2 - F_n Q + kQ^2/2, \qquad (1)$$

where Q is the configuration coordinate for the displacement of the DB, ε_0 the bond energy of the tetrahedral hybrid without distortion, k the stiffness of the oscillator, and F_n the force induced by the n electrons on the DB state (by convention, $F_0 = 0$ and $F_1 = F$). The level $(0/-)$ being resonant in the conduction band, we assume that

there is no supplementary force ($F_2 = F$) when a second electron is injected in the DB state due to its short lifetime. Indeed, the full width at half maximum (110 meV) of the $(0/-)$ resonance is large compared to the vibration energy of the DB (30 meV [15]). Following Huang-Rhys theory in the strong electron-vibration coupling regime [23], the energies of the tunneling peak maxima are given by $E(+/0) = E(1, Q_0) - E(0, Q_0)$ and $E(0/-) = E(2, Q_1) - E(1, Q_1)$ because, at low temperature, the system is at its minimum of energy before injection of an extra electron; i.e., $E(0, Q)$ $[E(1, Q)]$ is minimum for $Q = Q_0$ (Q_1). We deduce that $\Delta E = U$ in that particular case.

By using simple electrostatic arguments, $U = 1.2$ eV has been estimated for a DB at a free Si surface [22]. Our measured value (~ 0.75 eV) is smaller due to screening by the metallic tip. To check that hypothesis, we have performed self-consistent tight-binding calculations on spherical Si nanocrystals. We have introduced one DB at the nominally hydrogen passivated surface, and we calculate the variation of the DB energy level upon addition of a charge. The tight-binding method provides a very good description of the dielectric screening and allows us to study nonperiodic (to avoid long-range interactions) systems containing up to 1700 atoms. The Hamiltonian is written as $H = H^0 + W$, where H^0 is the bare Hamiltonian parameterized in Ref. [24] and W is the potential induced by the variations of charges. Since W varies slowly, only the diagonal matrix elements of W are considered: On an atom i, W_{ii} is given by $-e\sum_j V_{ij}$, where V_{ij} is the potential induced by the charge q_j on the atom j. For an isolated nanocrystal, V_{ij} is simply equal to q_j/R_{ij}, where R_{ij} is the distance between the two atoms ($V_{ii} = \upsilon_0 q_i$, where $\upsilon_0 = 10.6$ V represents the intra-atomic interaction [25,26]). The Hamiltonian is diagonalized and the net charge on each atom is deduced from the occupied states. The problem is solved iteratively until self-consistency, for two charge states of the DB.

The influence of the tip is simulated by a metallic plane perpendicular to the surface and lying at 1 nm from the DB. The metallic plane is described by the image charge method, i.e., $V_{ij} = q_j(1/R_{ij} - 1/R'_{ij})$, where R'_{ij} is the distance from the atom i to the image of the atom j with respect to the metallic plane. In all the cases, we obtain that the charging energy varies like $U_0 + b/R$, where R is the nanocrystal radius. The term b/R comes from the incomplete screening in the finite system [25], and U_0 is the charging energy in the limit $R \to \infty$. For the free nanocrystals, we obtain $b = 1.44$ eV $\cdot$ nm and $U_0 = 1.12 \pm 0.06$ eV, confirming previous estimations [22]. In the presence of a tip, we get $b = 1.29$ eV $\cdot$ nm and $U_0 = 0.82 \pm 0.06$ eV, in good agreement with experiments.

In summary, we have studied correlation effects in a single atomic orbital. We emphasize that this method can be applied to a wide range of quantized systems from single atoms and molecules to inorganic nanostructures. It is a prerequisite to ascertain that correlation effects occur when tunneling spectroscopic measurements are performed.

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